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ANODIC FILMS

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ABSTRACT

Surface layers are formed on many metals by anodic reaction. Such layers include the products of charge and discharge in many storage batteries, dielectric films used in electronic and optical circuits and display devices, layers responsible for passivity and corrosion protection, and films generated in metal shaping and finishing operations such as anodization, coloring, electropolishing, electrochemical machining and deburring. Anodic films are formed by solid-solid transformations or by dissolution-precipitation processes. Film properties and mechanisms of formation can be determined in situ by a number of optical techniques which have recently become available.

Anodic reactions involve the oxidation of materials by the withdrawal of electrons at a solid-electrolyte interface. The reaction products may be soluble or insoluble and can lead to the formation of anodic surface layers. Such layers are often different from those formed by chemical reactions because of the different mechanisms of formation involved. The electrical control of the oxidation potential allows one to generate very high concentrations (activities) of reaction products in the immediate vicinity of the surface and to select specific oxidation states of the products. With soluble reaction products, film formation often involves precipitation with nucleation and growth from a supersaturated solution, even if solubilities are very low; direct solid-solid transformation is the film formation mechanism otherwise involved.

The chemical properties of most metals in contact with liquid or gaseous media are determined by the properties of surface layers, many of which are of anodic origin. Surface layers which often form in an uncontrolled way are also of importance in metallic corrosion. Many anodic surface layers can be permeated by ions due to porosity or solid state ionic conductivity. Such layers are formed in many galvanic cells (batteries). The controlled change of the valence of materials by the withdrawal of electrons also occurs in the anodic formation of dielectric oxide layers of high perfection, long used in electrolytic capacitors and more recently, in integrated electronic circuits. In metal finishing, anodic surface layers are used for decorative purposes and corrosion protection; their presence is essential to achieve bright surfaces in electrochemical machining and polishing.

Experimental techniques which have become available in recent years have made it possible to advance the understanding of anodic film formation. Some of these techniques allow the observation of film growth in situ, starting with fractional monomolecular coverage, and the results can be used to derive information on the mechanism of film formation. These studies have also confirmed earlier indications that anodic films often consist of several layers and are of non-stoichiometric composition.

Since publication of the classical book, "Anodic Oxide Films," by L. Young in 1961 (1), no comprehensive summary on this most prominent kind of anodic films has become available and the field has greatly expanded since. More recent summaries of some topics can be found in different book series, particularly, "Oxides and Oxide Films," edited by J. W. Diggle, et al., (2) or "Physics of Thin Films," edited by G. Hass, et al. (3). Another book of fairly recent origin is that by A. K. Vijh on "Electrochemistry of Metals and Semiconductors," (4). A vast amount of thermodynamic information is contained in the "Atlas of Electrochemical Equilibria in Aqueous Solutions," by M. Pourbaix (5). L. Young

and co-workers have written a more recent chapter on anodic oxide films (6). The Anodic Behavior of Metals is also discussed in a review chapter by T. P. Hoar (7).

ENERGY CONVERSION AND STORAGE

All the conventional, rechargeable batteries (secondary or storage batteries) involve the transformation of surface layers in the charge and discharge process. In general, the reactions occur on the interior surface of porous electrodes. Recent books, (8) and reviews (9) of battery technology are available.

Despite a long-established technology,(10), the detailed processes in lead-acid batteries are still not completely understood. The nickel electrode is the same in iron-nickel oxide and cadmium-nickel oxide (11) batteries. Reactions in the zinc-nickel oxide battery, which is presently being developed, involve the precipitation of zinc oxide from zincate solution. The zinc-silver oxide battery is an established primary, high-energy battery, presently being developed as a secondary battery. In the aluminum-air battery, aluminum oxide is formed in a crystallizer outside the galvanic cell.

Ambient-temperature lithium batteries, which employ different nonaqueous electrolytes, very much depend on the formation of surface layers on the lithium electrode (12) for their functioning. On thermodynamic grounds lithium would be expected to react spontaneously in corrosion reactions with most solvents and solutes used. Surface layers largely prevent such reactions and therefore provide acceptable shelf-life; however, after prolonged periods at open circuit, power delivery by the battery is often impaired by a phenomenon called voltage delay, attributed to overly thick protective layers which must be partially removed for satisfactory operation. So far, ambient temperature lithium batteries are primary batteries and it is increasingly recognized that surface layers are responsible for their lack of rechargeability. The use of lithium in an aqueous battery is also made possible by the formation of a protective surface layer (13).

ELECTRONIC COMPONENTS AND MATERIALS

Much of the early interest in anodic surface layers has been centered in their use in capacitors. Such films are also called barrier layers; metals from which they are formed are called valve metals because of the rectifying properties of the layers in some electrolytes. Oxides on aluminum, tantalum, and niobium are primarily used as dielectrics. More recently, the formation of dielectric films on semiconductors, such as silicon, germanium, and gallium arsenide, has become of interest (14). Questions of dielectric breakdown have been investigated in connection with these applications and with film formation limitations.

Optical properties of dielectric layers, such as electrooptic and electrostrictive effects in tantalum oxide (15) are being investigated for potential use in optical signal processing (16) and display, as are electrochromic reactions in which oxide films are reversibly colored and bleached by anodic and cathodic reactions (17).

PASSIVITY AND CORROSION

Because of the significance of economic losses caused by corrosion, studies of corrosion processes have been conducted intensively for a long time and are summarized in several current textbooks (18,19). Corrosion involves coupled anodic and cathodic processes, usually on neighboring surface elements.

Passivating films were originally defined as very thin electronically conducting layers which inhibit anodic metal dissolution (7). The first two conditions are often not obeyed in the present use of the term "passivity." The onset of anodic passivity is characterized by a large drop in dissolution current over a narrow range of potentials. Passivation has been reviewed recently (20).

Corrosion inhibitors have been shown to change oxide films on iron. Pitting corrosion and stress corrosion cracking appear to involve the rupture of protective surface layers.

The breakdown of protective and passivatin layers is of great practical interest. Such breakdown is often caused by the presence of halide ions. Passive layers can also be removed by anodic polarization, which is desireable for metal dissolution in batteries.

METAL SHAPING AND FINISHING

The old-established technology of electrochemical polishing of metals (21) has only rather recently been investigated in detail (22). Electropolishing requires a surface condition intermediate between normal (active) dissolution and passivity (23). Although electropolishing is typically

associated with transport limitations in the liquid phase, anodic films also play a role and have been shown to be usually present when polished surfaces result from electrochemical machining (24). Due to their resistive nature, such films are also important for dimensional control in electrochemical machining (25) and electrolytes favoring film formation have been preferred for this reason (26). Bright surfaces can, however, also be obtained in chloride solutions under conditions where a salt film is precipitated (27). Coloring of many metals is also accomplished by anodic treatment or by the incorporation of dyes into porous oxide layers. Best known is the anodizing and coloring of aluminum (28).

FILM FORMATION AND FILM PROPERTIES

Mechanisms of anodic film formation are usually quite specific for the materials and conditions involved and their elucidation is, in many cases, still in progress. The importance of the solubility of electrode materials in the formation of surface layers on battery electrodes was recognized some time ago (29).

The formation of lead sulfate on lead in sulfuric acid proceeds via a solution precipitation mechanism (30). Anodic film formation on iron has been proposed to proceed via dissolution-precipitation in a first step and solid state ion and electron migration in a second step (31), and results in a dual-film structure. The anodic oxidation of nickel results in the formation of $Ni(OH)_2$ (32), which can be further oxidized to NiOOH. During film formation, the continuous breakdown of a compact inner film has been proposed to generate Ni^{2+} ions which form a porous outer film of NiOOH (33). Multi-layer films have been found to result from the anodic oxidation of cadmium in alkaline solutions (34). A combined solid-state and solution-precipitation mechanism has been proposed for the formation of the resulting $Cd(OH)_2$ layer (35).

The anodic formation of silver oxide in alkaline solutions has been investigated by many authors. The use of multi-dimensional film formation models for the interpretation of time-dependent ellipsometer measurements during film growth resulted in a proposed multi-layer film structure (36). This model postulated the formation of secondary crystals on top of a compact adsorbed layer, followed by hydrated and colloidal layers facing the solution, in analogy to the type-I and type_II layers identified by R. W. Powers and M. W. Breiter, on Zinc (37). Many reactions other than oxidation result in anodic films on silver. Prominent among them is silver chloride which is used as a common reference electrode.

There is little argument that anodic formation of zinc oxide in alkaline solutions involves dissolved zincate at supersaturated concentrations (38). A dense passivating (type-II) layer has been identified by microscopy underneath a porous precipitate (type-I) layer (37). Transfer of OH^- or the formation of compact ZnO have been proposed as passivation mechanisms at low and high current densities, respectively (39).

The properties of surface layers formed on lithium in different nonaqueous electrolytes have been accounted for by a solid electrolyte interphase model (40). The composition of many of these layers is still uncertain. In alkaline aqueous solutions, lithium is partially protected by an inner oxide/hydroxide and an outer hydrate layer (41).

Anodic barrier layers grow by the migration of both anions and cations in the film. Transference numbers in tantalum oxide have been measured by the incorporation of noble gas isotope markers (42). A dual-film structure with a thin dense inner layer and a thick porous outer layer has long been suggested (7) and was found in ellipsometer measurements (43). Very reproducible film thicknesses of barrier layers can be achieved under prescribed conditions; an anodization constant of 15 Å per volt has been reported for tantalum oxide (44). Because of the ease of preparation tantalum oxide films are now widely used as thickness standards in surface science.

Electrical breakdown of aluminum oxide and tantalum oxide during film growth follows an avalanche breakdown model (45). Typically, breakdown voltage is independent of applied current density, but depends on crystal orientation. Switching phenomena in thin films involve a partial, reversible breakdown (46).

The mechanisms by which passivating surface layers are formed varies greatly for different materials. For iron in carbonate solution, active dissolution has been found to result in Fe^{2+} ions while the passive layer consists of Fe_2O_3; a two-layer film of ferrous oxide has been found to form in alkaline solutions (47). Salt films have been found to preceed passivating oxide film formation on iron in perchloric and sulfuric acid (48). A monolayer of PtO, Au_2O_3, Co_2O_3, and FeO is sufficient for passivation, while several monolayers of Ni_2O_3, CuO, Ag_2O and TiO_2 and thick films of Ag_2SO_4 and PbCl are required (7).

Film formation on copper has also been extensively studied. In alkaline solutions, a monovalent copper species is involved in nucleation and growth of a cuprous oxide film (49).

The anodic breakdown of passive films has been explained in semi-conductor terminology by the adsorption of anions which results in formation of acceptor levels; a point defect model has been used to explain the chemical breakdown by the action of halide ions (50). Oscillatory behavior due to periodic formation and breakdown of anodic films has been observed with copper (51), nickel and chromium alloys.

The formation of anodic films in the dissolution of iron and steel has been found to depend greatly on the anions in the solution. In nitrate a protective, electronically conducting film of Fe_3O_4 is formed at low current densities; this film then breaks down at higher current densities (52). Passivation by a salt layer occurs in the dissolution of steel in sulfate and perchlorate solutions (53). The formation of a protective salt layer on an anodically dissolving metal has been analyzed theoretically (54). For the electropolishing of copper in phosphoric acid, the solubility of phosphate has been found to be exceeded at the interface when an oxide film of 13 to 124 Å thickness develops (55). Iron and nickel in sodium chloride solutions produced etched surfaces in the active dissolution regime and bright surfaces in transpassive dissolution. Passivating salt layers have been found to show non-ohmic resistance, with a voltage drop which is often independent of current density (27).

EXPERIMENTAL TECHNIQUES

Among the experimental techniques for the study of anodic films, optical methods occupy a special position because most of them can be used on electrodes while they are immersed in electrolyte (56). All the electrochemical measurements, including the more recently introduced impedance measurements (57), are also conducted in situ. Several summaries of the optics of thin films are available (58), but the field is still under development. A comprehensive treatment of ellipsometry has been prepared by R.M.A. Azzam and N. M. Bashara (59). Several introductory (60) and review articles (61) on ellipsometry are also available. Since the early use of ellipsometry, the interpretation of measurements has been greatly advanced; some of these advances are documented in the proceedings of four international ellipsometry conferences, the last proceedings available are from the one held in 1971 (62).

Reflection spectroscopy is another in situ technique for surface layers (63). To increase sensitivity, multiple reflections and electroreflection, in which one measures changes in reflectivity due to changes in electrode potential, have been used. Of recent origin for the study of surface layers is the use of Raman spectroscopy (64), particularly the surface-enhanced Raman scattering (65) which offers sensitivity to fractional monolayer coverages, but is restricted to the highly reflecting metals, particularly silver.

Thin film interference is an old but still very useful optical technique for the observation of surface layers (66). Barrier layers on aluminum, tantalum, niobium, and zirconium have been observed by this technique. Anodic oxides on uranium and bismuth also show interference colors.

Optical microscopy is also a very useful technique to observe anodic film formation (37), and has been adapted to look at a single-pore model (67). Scanning image microscopy (68) primarily in the form of scanning electron microscopy, electron and ion microprobe analysis (69), and scanning transmission electron microscopy are very powerful tools for surface analysis, as are other experimental techniques of modern surface science. These are ex situ techniques which require the transfer of the electrode from the liquid to an ultrahigh vacuum environment. Even if this transfer is accomplished without exposure to the atmosphere, it involves a significant period of time in which potential control is not possible and corrosion reactions may occur. The removal of solvent can also result in the collapse of porous film structures and the change in composition due to the removal of hydrate water.

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